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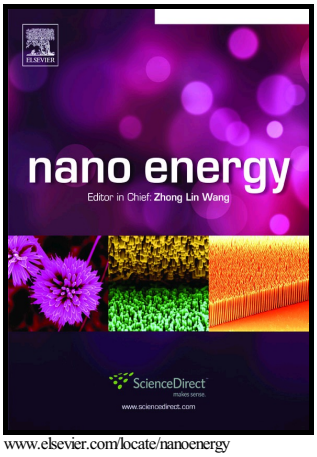

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Electrochemical Reduction of CO_2 on Compositionally Variant Au-Pt Bimetallic Thin Films

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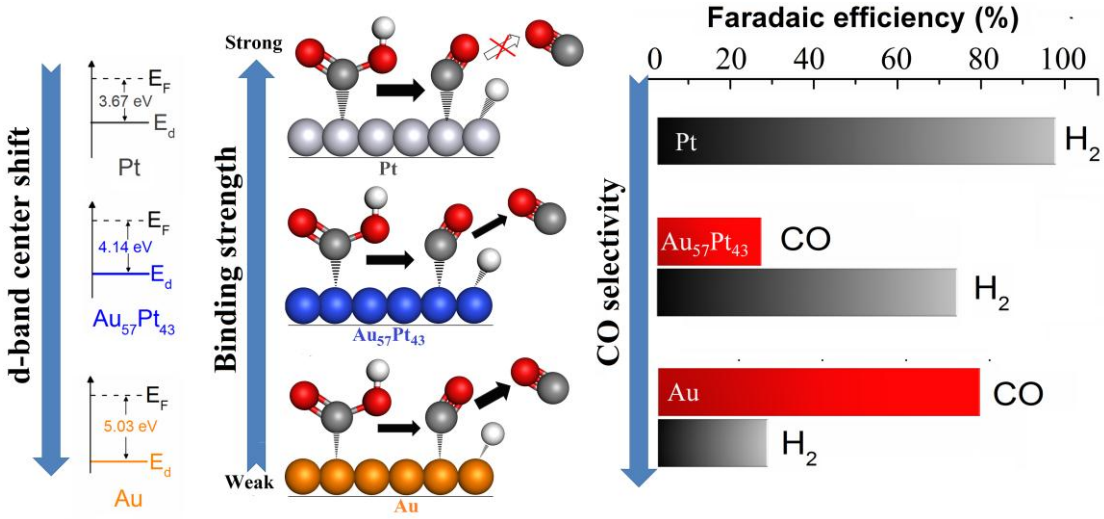
ABSTRACT

The electrocatalytic reduction of CO_2 on Au-Pt bimetallic catalysts with different compositions was evaluated, offering a platform for uncovering the correlation between the catalytic activity and the surface composition of bimetallic electrocatalysts. The Au-Pt alloy films were synthesized by a magnetron sputtering co-deposition technique with tunable composition. It was found that the syngas ratio ($CO:H_2$) on the Au-Pt films is able to be tuned by systematically controlling the binary composition. This tunable catalytic selectivity is attributed to the variation of binding strength of COOH and CO intermediates, influenced by the surface electronic structure (d-band center energy) which is linked to the surface composition of the bimetallic films. Notably, a gradual shift of the d-band center away from the Fermi level was observed with increasing Au content, which correspondingly reduces the binding strength of the COOH and CO intermediates, leading to the distinct catalytic activity for the reduction of CO_2 on the compositionally variant Au-Pt bimetallic films. In addition, the formation of formic acid in the bimetallic systems at reduced overpotentials and higher

yield indicates that synergistic effects can facilitate reaction pathways for products that are not accessible with the individual components.

Graphical Abstract



The electrocatalytic reduction of CO_2 on Au-Pt bimetallic catalysts with different compositions was evaluated, offering a platform for uncovering the correlation between the catalytic activity and the composition of bimetallic electrocatalysts.

Keywords: CO_2 conversion; bimetallic catalysts; Au-Pt alloy thin films; electrocatalysis

1. Introduction

Converting CO_2 electrochemically into fuels and valuable chemicals has great potential for the utilization of captured CO_2.[1–6] For a sustainable production of fuels and value-added chemicals with zero carbon emission, renewable electricity sources can be used to power the electrocatalytic reduction of CO_2.[1,7] One of the main challenges for achieving this goal is to develop a cost-effective electrocatalysts, which is capable of reducing CO_2 efficiently with controllable selectivity and long-term stability. Primary investigations studied various

polycrystalline metallic materials for the electrochemical reduction of CO_2 in aqueous electrolyte.[2,3,8–11] While several polycrystalline metal catalysts have been identified with the capability to electrocatalytically reduce CO_2, the high overpotential required for driving selective CO_2 reduction with suppressed H_2 evolution and the fast catalytic deactivation in favor of H_2O reduction significantly limits the potential for large-scale applications.[12,13]

The electrocatalytic reduction of CO_2 is a multi-step reaction with many reaction intermediates (such as COOH and CO) that are bound to the catalyst surface. The binding strength of these intermediates plays a key role in determining the selectivity to form specific reaction products.[14–17] Recently, bimetallic electrocatalysts have attracted considerable attention as a promising approach to improve the catalytic activity and selectivity of CO_2 reduction.[18–24] Alloying two metals can alter the electronic structure of a catalyst, which in turn alters the binding strength of intermediates due to both electronic and geometric effects.[19,25] Furthermore, the electronic properties of alloys could be due to the combination of the individual contribution of each metal, or a rehybridization of the two metals' orbitals. Density functional theory (DFT) has been utilized for calculating the binding energy of multiple intermediates on various alloys, giving a theoretical basis for developing suitable bimetallic alloy catalysts with high catalytic activity for a desired product.[14–16,26]

Experimentally, it has been demonstrated that the interaction of the two different metal atoms in a bimetallic alloy could significantly influence the catalytic activity and selectivity in the electroreduction of CO_2. Recently, Koper *et al.*[27] reported that bimetallic Pd-Pt alloy nanoparticles exhibit a very low onset potential for the reduction of CO2 to HCOOH of ~ 0 V vs. the reversible hydrogen electrode (RHE) and a high faradaic efficiency (FE) of 88% for HCOOH formation at -0.4 V vs. RHE. In addition, Takanabe *et al.*[18] discovered that a nanostructured Cu-In bimetallic alloy prepared by the in situ electrochemical reduction of Cu_2O in $InSO_4$ electrolytes is able to reduce CO_2 to CO with a FE of 85% at -0.6 V vs. RHE.

Furthermore, the dramatically improved FE for the reduction of CO_2 to CO has also been achieved on nanostructured Cu-Sn and Cu-Pd bimetallic catalysts at reduced overpotentials.[20,28] While impressive progress has been made on the improvement of the catalytic activity and selectivity for the reduction of CO_2 on alloy catalysts, the fundamental understanding of the correlation of the composition of bimetallic catalysts with the catalytic activity remains unclear. This discrepancy largely comes from the fact that many of the studied catalysts for CO_2 reduction are nanostructured materials, which make it difficult to distinguish the effects of bimetallic composition and surface morphology (each of which can contribute to altered CO_2 reduction performance). Furthermore, synergistic effects of bimetallic systems have not been explained by existing models due to the complexity of the nanostructured surfaces and compositional variation.

Au is the most active metal electrocatalysts for the reduction of CO_2 to CO, however, the catalytic activity on Au is still limited by the activation of CO_2 to stabilize COOH.[17] In contrast, Pt provides favorable activation and conversion of CO_2 to adsorbed CO (limiting step is CO desorption).[17] Herein, we present the first exploration of the electrocatalytic reduction of CO_2 on Au-Pt bimetallic thin films with controllable compositions and planar morphology. These bimetallic planar films provide an ideal platform for investigating the electronic and synergistic effects on the binding strength of intermediates and the formation of final products by tuning the composition of bimetallic catalysts while keeping the surface morphology consistent. A systematic experimental and theoretical investigation elaborates the mechanism of the effect of binary catalyst composition on the catalytic activity and selectivity of CO_2 reduction, revealing that major products formation (H_2 and CO) closely follows the surface compositional changes, while the formation of HCOOH was found to occur at lower potentials and with significantly improved amounts. Thus, the surface composition and

bimetallic synergy of two metals both contribute to the overall CO_2 reduction performance of Au-Pt electrocatalysts.

2. Results and discussion

2.1 Fabrication and characterization of bimetallic Au-Pt films

For obtaining high purity Au-Pt bimetallic films, Au-Pt films were deposited by a magnetron sputtering co-deposition technique (separated targets) at an argon pressure of 0.3 Pa, as shown in Fig. S1. In this co-deposition process, the deposition rates of the two target materials (Au and Pt) were manipulated by adjusting the deposition power, respectively, for synthesizing the controllable compositions of binary metals. The composition of binary films will be hereafter expressed by the atomic ratio of Au and Pt ($Au_{100-n}Pt_n$, $0 \leq n \leq 100$). In addition, the thickness of the Au-Pt films were controlled by deposition time, and the cross-sectional scanning electron microscopy (SEM) image (Fig. S3) indicates that the Au-Pt binary electrocatalyst was comprised of ~ 60-70 nm thick film.

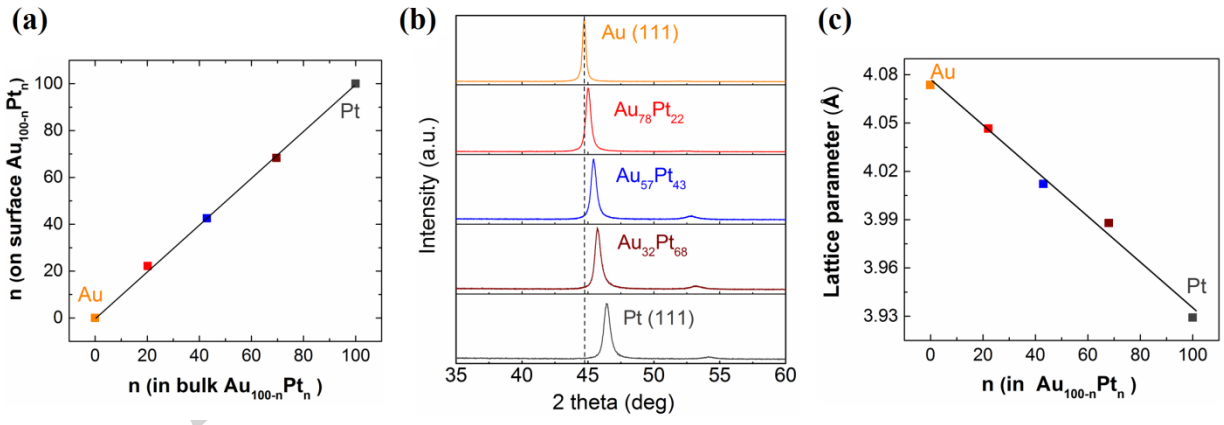


Fig. 1. Characterization of Au-Pt bimetallic films. (a) A comparison of surface composition with bulk composition of AuPt film measured by XPS and EDS, respectively. (b) XRD patterns of pure Au (orange line), pure Pt (gray line) and $Au_{100-n}Pt_n$ bimetallic films. (c) Variation of the lattice parameter of the Au-Pt bimetallic alloys as a function of the Pt content.

To confirm the surface composition of the deposited Au-Pt bimetallic films, X-ray photoelectron spectroscopy (XPS) measurements were performed. It was found that the

surface atomic ratio of Au to Pt in the Au-Pt bimetallic film was tuned by altering the deposition rate of magnetron sputtering (Table S1). It has been reported that Au could segregate to the surface of binary films, which is caused by the low surface free energy of Au, resulting in slightly enriched Au in binary film.[29] Here, the bulk composition (Table S2) of the deposited Au-Pt bimetallic film were characterized by Energy-dispersive X-ray spectroscopy (EDS). The comparison of the bulk and surface composition of binary films is presented in Fig. 1a, which reveals the composition of the Au-Pt binary films was consistently identical up to the outermost layer of the films, indicating no obvious Au segregation at the surface of the binary films prepared by magnetron sputtering. The observation of no Au segregation at the surface is consistent with the previous work on Au-Pt bimetallic films fabricated using pulsed laser deposition.[30] Importantly, the surface composition of the Au-Pt films was maintained even after 2 hours of electrolysis (Table S3).

X-ray diffraction (XRD) measurements were conducted for verifying the formation of the Au-Pt alloys. As noted in the XRD patterns (Fig. 1b), all compositions of the samples exhibited only one dominant diffraction peak which can be assigned to the diffraction of the (111) plane from the fcc crystal structure and the (111) peak position gradually shifted to larger 2θ with an increase of Pt content, indicating the formation of the Au-Pt bimetallic alloys.[29] The shift of the (111) peak towards larger 2θ with increasing Pt content is attributed to the reduced lattice parameter of Au-Pt alloy caused by the incorporation of Pt (the lattice parameter of the alloy is between the pure Au and Pure Pt). Here, the lattice parameter of Au-Pt alloys (Table S4) was extracted according to the XRD patterns and Bragg's law (Eqs. S1). A plot of the lattice parameter as a function of Pt content in the Au-Pt bimetallic films is displayed in Fig. 1c, which includes the lattice parameter of pure Au (0.40736 nm) and pure Pt (0.39290 nm) for comparison. A linear relationship between lattice parameter and the Pt content of Au-Pt films was observed (Fig. 1c), which is the typical

characteristic of alloying based on Vegard's law.[30,31] These results indicate that Au-Pt alloys were formed over the whole composition range without Au segregation at the surface.

2.2 Electrocatalytic CO_2 reduction activity.

The electrochemical reduction of CO_2 on the Au-Pt bimetallic films with different compositions were performed in a CO_2-saturated 0.1 M $KHCO_3$ (99.95%) electrolyte (pH = 6.83) at room temperature and atmospheric pressure. The CO_2 electroreduction was conducted in an electrochemical cell, which is separated into working and counter electrode compartments by a Nafion-115 proton exchange membrane for preventing the oxidation of the CO_2 reduction products. The cathodic compartment was continuously purged with CO_2 at a constant flow rate, venting directly into the gas-sampling loop of a gas chromatograph (GC) for periodically quantifying the gas-phase products. To analyze liquid products produced in the CO_2 reduction, the CO_2 reduction electrolyte was collected after completion of the electrolysis experiments and then detected by ^1H nuclear magnetic resonance (NMR).[32]

The comparison of the electrocatalytic activity of the Au-Pt bimetallic alloys with different compositions is presented in Fig. 2. CO and H_2 were detected as the major products of CO_2 reduction on these Au-Pt bimetallic alloys (Fig. 2). At a fixed potential of 0.65 V vs. RHE, CO formation was not detected on pure Pt, and the highest CO faradaic efficiency of ~77% was observed on pure Au. Interestingly, the Au-Pt bimetallic alloys exhibited a gradually enhanced FE for CO formation as the Au content increased, simultaneously accompanying with decreased FE for H_2 evolution, which reveals that the syngas ratio ($CO:H_2$) could be tailored in the electroreduction of CO_2 at a fixed potential by systematically tuning the composition of the Au-Pt bimetallic films.

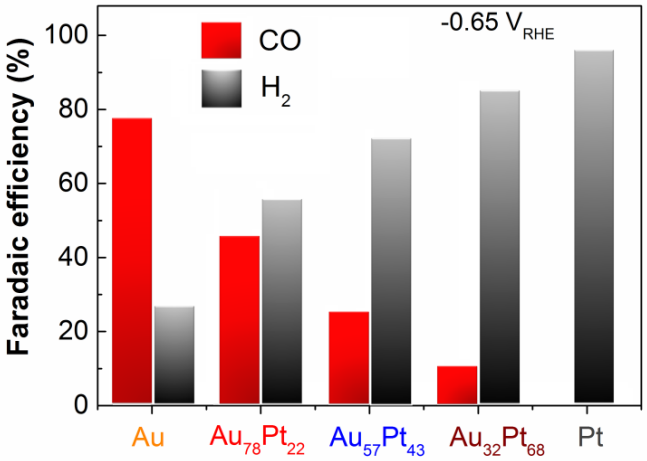


Fig. 2. Faradaic efficiency for CO on Au-Pt bimetallic alloys with different compositions at 0.65 V versus RHE in CO_2-saturated 0.1 M $KHCO_3$ electrolyte (pH= 6.8).

To gain a deeper understanding of the trend of the electrocatalytic activity of CO_2 reduction on Au-Pt alloys with different compositions, the FE for the major products was plotted at various potentials (Fig. 3). With increasing overpotentials, the Au-Pt bimetallic catalysts with various compositions all experienced a gradually increased FE for the reduction of CO_2 to CO, while the peak FE for CO on pure Au was achieved at -0.6 V vs. RHE and then a gradual decrease in the FE for CO was detected with further increasing overpotentials. In addition, the opposite tendency in FE for CO and H_2 was also observed on the Au-Pt bimetallic films with different compositions at various potentials. As displayed in Fig. 3a and 3b, the increase in the FE for CO formation followed the correspondingly reduced FE for H_2 evolution with increasing Au incorporation at various potentials. In this study, during the various potential tests for CO_2 reduction, CO formation on Pt was only detected at 0.7 V vs. RHE with a very low FE of 1%, and the CO formation on $Au_{32}Pt_{68}$, $Au_{57}Pt_{43}$ and pure Au was able to be detected at 0.4 V, 0.35 and 0.3 V vs. RHE, respectively, which implies the decreased overpotential for the reduction of CO_2 to CO with increasing Au content of Au-Pt bimetallic catalysts (Fig. 3a). Furthermore, a plot of the partial current density for CO formation as a function of potential in Fig. 3c also reveals a positive shift for the onset potential in the reduction of CO_2 to CO with incorporating more Au into binary films. These results indicate

that the catalytic activity for the reduction of CO_2 to CO and the competing H_2 evolution can be tuned on the Au-Pt bimetallic films by systematically controlling the atomic ratio of Au/Pt.

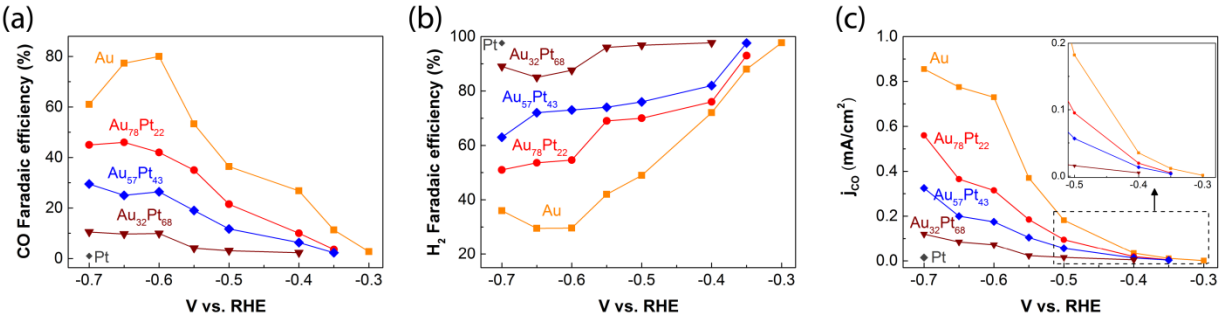


Fig. 3. Comparison of the electrocatalytic performance of AuPt bimetallic alloys with different compositions. Faradaic efficiency for CO (a) and H_2 (b) on AuPt bimetallic alloys with different compositions at various potentials in CO_2-saturated 0.1 M $KHCO_3$ electrolyte (pH= 6.8). (c) Partial current density for CO at various potentials. No detected CO formation on Pt film.

In addition to the observed major products, formate was also detected as a liquid product. As presented in Fig. 4, the formation of HCOOH (FE of 1.4%) started to be detected on pure Au at -0.6 V vs. RHE, and at a less negative potential of -0.55 V vs. RHE, a FE of 2% for HCOOH was observed on $Au_{78}Pt_{22}$ (Fig. 4). Notably, for driving the electrocatalytic reduction of CO_2 to HCOOH, a potential of -0.5 vs. RHE was required on the $Au_{57}Pt_{43}$, which is a positive shift of 100 mV and 50 mV in comparison with pure Au and $Au_{78}Pt_{22}$, respectively. These findings imply that the Pt content (<50 at.%) in Au-Pt bimetallic catalysts may facilitate the electrocatalytic reduction of CO_2 to HCOOH formation at a reduced overpotential. With further increasing the Pt composition, the potential required for driving the reduction of CO_2 to HCOOH formation shifted back to a more negative potential (0.6 V and 0.65 V vs. RHE were required for $Au_{32}Pt_{68}$ and Pt, respectively). This observation may be due to the synergy of having Au and Pt atoms next to each other, which provide binding sites for reaction intermediates which favor the formation of HCOOH. All the above results indicate that the catalytic activity and selectivity for major products formation in CO_2 reduction is strongly linked to the surface composition of the Au-Pt bimetallic alloys, while

the synergy of the two metals allows the increased production of minor products at lower overpotentials.

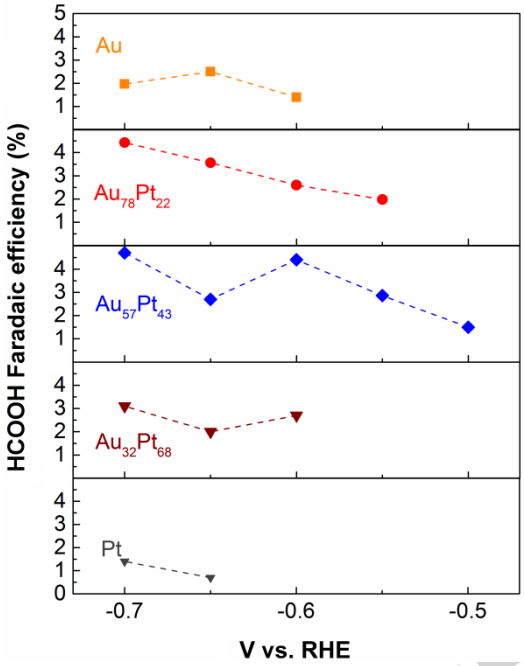


Fig. 4. Faradaic efficiency for HCOOH formation at various potentials in CO_2-saturated 0.1 M $KHCO_3$ electrolyte.

To gain further insights into the influence of the binary composition on the catalytic activity of CO_2 reduction, it is critical to distinguish the electronic effect and the geometric effect.[19,25] The electronic effect is linked to the change of electronic structure that is tuned with surface composition of bimetallic catalysts, which results in the variation of the binding strength of intermediates. In addition, the geometric effect that is correlated with the atomic arrangement at the active site which has a significant influence on the interaction between adsorbed species and the surface atoms.[19] In our study, the surface roughness was analyzed by atomic force microscopy (Fig. S5, all films on polished Si substrates had a roughness of 0.3 - 0.5 nm), showing magnetron sputtering is able to deposit uniform flat surface layer for all different compositional alloys, which implies that the variation of the catalytic activity with changing the bimetallic composition should be only related to the surface electronic effect.

For the effect of the electronic properties on the catalytic activity and selectivity, d-states (that are close to the Fermi level) of transition metals play an important role in the binding strength of adsorbed species on the surface.[25,31,33] The higher energy of d-states leads to the stronger interaction with adsorbed intermediates.[33] Thus, alloying two metals may alter the average energy of the d-electrons of the catalyst surface, which is correlated with the variation of the binding strength of intermediates, leading to the change of catalytic activity and selectivity. Of particular note, it has been reported that value of d-band center can be used to represent the average energy of the d-electrons.[33]

In order to reveal the variation of the average energy of the d-electrons with the bimetallic composition, high-resolution surface valence band XPS measurements were performed on Au-Pt bimetallic films. The surface valence band XPS spectra as a function of composition of the Au-Pt bimetallic films is presented in Fig. 5a (the observed surface valence bands could be from the combination of Au and Pt, or a rehybridization of the two metals' orbitals). The position of the d-band center of Au-Pt bimetallic films was determined according to Equation S(2), and was labeled with colored vertical lines in Fig. 5a, which indicates an obvious change of the d-band center with different atomic ratios of Au/Pt. The energy of the d-band center as a function of Pt content shown in Fig. 5b implies that pure Pt has the closest d-band center (E_d=3.67 eV) relative to the Fermi level (E_F). Notably, the d-band center of Au-Pt bimetallic films was shifted away from the Fermi level (E_F) with gradually increasing Au content, correspondingly weakening the binding strength of intermediates on the surface, which is consistent with the reported bimetallic Au-Pt alloys.[31]

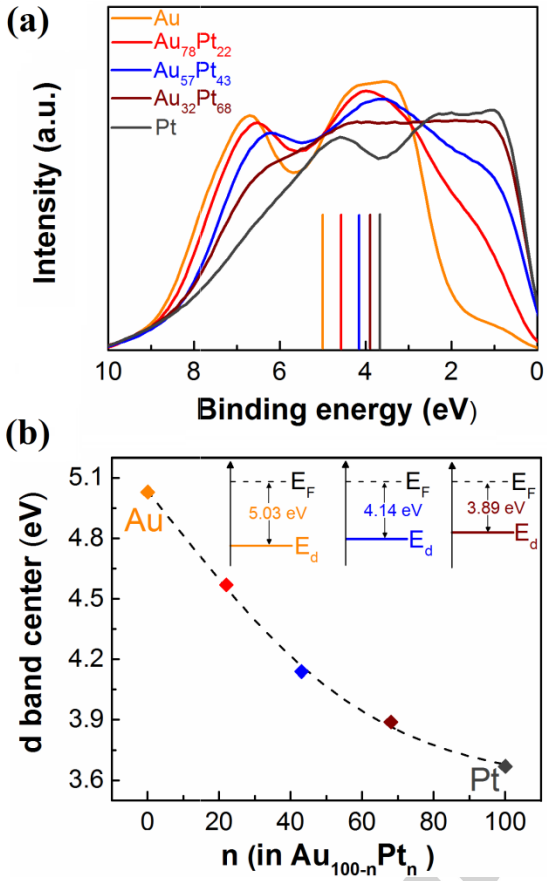


Fig. 5. Electronic properties of Au-Pt bimetallic films. (a) Comparison of surface valence band XPS spectra of Au-Pt bimetallic films with different composition (the binding energy is the value of $|E-E_F|$). The color line in the center represents the position of d-band center of the corresponding Au-Pt film. (b) Energy of d-band center as a function of Pt content. The inset shows the d-band center (E_d) position of Au and Au-Pt alloys with respect to the Fermi level.

Based on the catalytic CO_2 reduction performance of Au-Pt bimetallic films, we propose a mechanism to correlate the binding strength of COOH, CO and H intermediates on Au-Pt bimetallic films with the d-band center position relative to the Fermi level, as displayed in Fig. 6. For Pt, the E_d is very close to E_F (3.67 eV), which corresponds to the strongest binding strength of COOH and CO, indicating that the CO_2 activation for stabilizing COOH intermediate and the formation of adsorbed CO are facile. However, the desorption of CO from the surface is limited due to the strongest binding strength of CO on Pt (Fig. 6), which corresponds to the very low catalytic activity for the reduction of CO_2 to CO (Fig. 3a). This result is consistent with DFT simulation work for CO_2 reduction on Pt.[17] With increasing

Au composition of Au-Pt bimetallic films, the E_d moves away from E_F by getting more d-electrons from Au,[31] which reduces the binding strength of COOH and CO with gradually increasing Au content, resulting in gradually increased catalytic conversion of CO_2 to CO. The highest value of E_d (5.03 eV) was detected on pure Au, which offers weaker binding strength for COOH and CO, which is the optimum binding strength among transition metals for the reduction of CO_2 to CO,[17] corresponding to the highest catalytic activity for CO_2 reduction to CO on Au among the catalysts studied here.

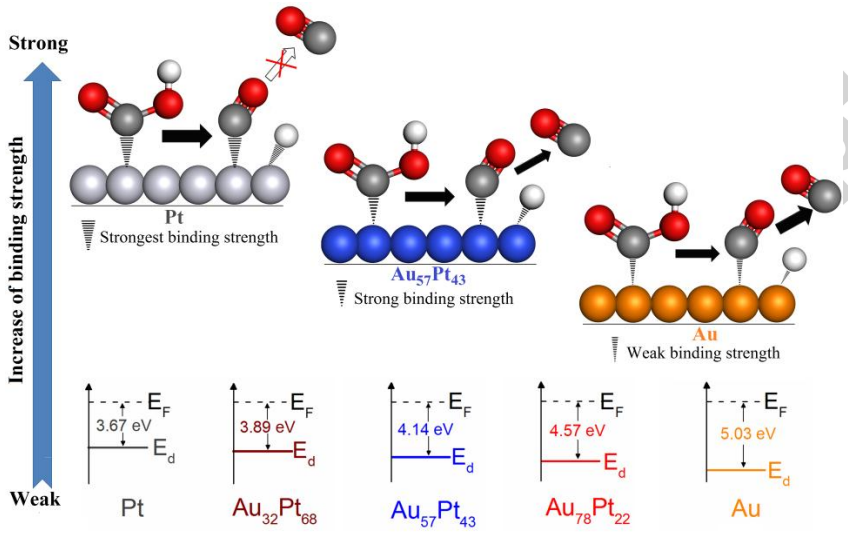


Fig. 6. Schematic illustration of binding strength of COOH, CO and H intermediates on Au-Pt bimetallic catalysts as a function of the d-band center position.

The above discussion indicates that the binding strength at a mixed site is the average of the properties of the constituents, which likely implies that the binding strength for intermediates on the Au-Pt bimetallic films are correlated linearly with each other with tuning the binary composition, corresponding to the gradually enhanced catalytic activity for the reduction CO_2 to CO with increasing Au content.

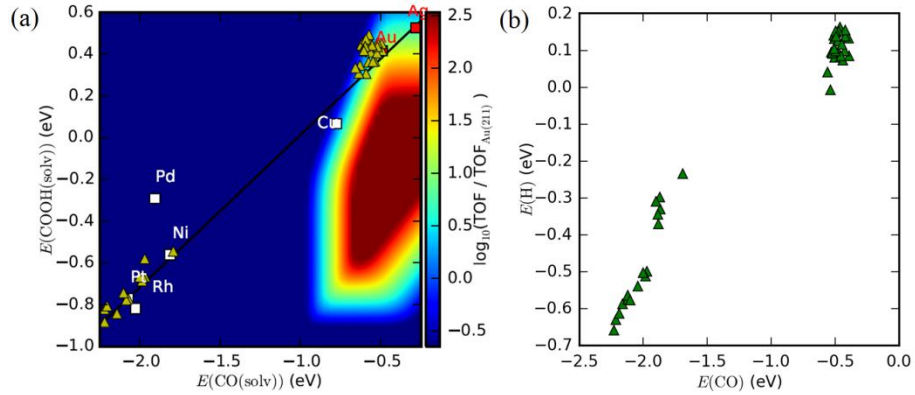


Fig. 7. (a) COOH and CO binding energies of Au-Pt (211) steps calculated from DFT shown over an activity map for CO production. (b) Correlation of CO and H binding energies on Au-Pt (211) steps.

The binding energies of the reaction intermediates on Au-Pt bimetallic surface were further investigated by DFT simulations. The binding energies of COOH and CO intermediates on the Au-Pt alloys are shown in Fig. 7a together with the rate of CO_2 reduction to CO based on a previously published micro-kinetic model.[17] According to this model, optimum activity for CO production is obtained for appropriate binding energies of COOH and CO, which simultaneously allow facile CO_2 activation and CO release. The catalytic activity on late transition metal and coinage metal surfaces is limited by a correlation between COOH and CO binding energies. The Au-Pt alloys studied here follow the same correlation between COOH and CO binding energies as discovered previously.[17] In addition, the variation in catalyst activity for CO production is linked to the change of hydrogen binding energy that is responsible for H_2 production,[34] due to a correlation between CO and H binding energies as presented in Fig. 7b. Furthermore, the variation of electronic properties on bimetallic surfaces are induced by strain and ligand effects.[35] We find no correlation between alloy lattice constants and binding energies of COOH, CO, H on Au-Pt alloy (Fig. S7). However, the electronic ligand effect plays a significant role, which may lead to Au atoms in Au-Pt alloys binding intermediates stronger than pure Au and Pt binding intermediates weaker than pure Pt, implying that the binding energies of intermediates on the Au-Pt alloy films lie in between

pure Pt and pure Au. This result is consistent with our experimental work. In addition, the shift of the d-band center away from the Fermi level with increasing Au composition is also found from DFT calculation (Fig. S8).

This exploration of the electronic effect on the catalytic activity for CO_2 reduction in the bimetallic system suggests that the binding strength for intermediates on Au-Pt bimetallic films likely follows the scaling relation, which is also in agreement with the previous DFT simulation work for Au-Pd alloy surfaces (a linear relationship is obtained between the adsorption strength of intermediates and the composition of alloy).[25] In addition, it was reported that although the dramatically improved FE for the reduction of CO_2 to CO is achieved on nanostructured Cu-In and Cu-Sn bimetallic catalysts at the reduced overpotentials, In and Sn deposited on flat Cu catalysts experienced a predominant H_2 evolution under similar conditions.[18,20] The significantly improved catalytic activity for CO_2 reduction only observed on the nanostructured Cu-In and Cu-Sn bimetallic surfaces is mainly ascribed to the synergistic geometric and electronic effects. It has been demonstrated that the geometric effect which could lead catalysts to deviate from the scaling relation has a significant effect on the adsorption of intermediates.[19,25] Thereby, it seems that a solely electronic effect of bimetallic alloys may not be enough to significantly break the scaling relation for dramatically improving the electrocatalytic reduction of CO_2. The atomic arrangement (nanostructure) should be also considered to design a bimetallic catalyst for the electroreduction of CO_2, which may be attributed to the synergistic geometric and electronic effects that contributes to the high-performance of bimetallic catalysts.

3. Conclusion

In summary, Au-Pt bimetallic thin films with tunable compositions were prepared with a uniform morphology, offering a platform for understanding the electronic effect on the catalytic activity for CO_2 reduction in a bimetallic system. The Au-Pt binary films exhibited a

gradually improved catalytic activity for the reduction of CO_2 to CO with increasing the Au content, which is attributed to the variation of electronic properties caused by changing binary composition. We show that the d-band center was gradually shifted away from the Fermi level with increasing Au content, which weakens the binding strength of COOH and CO, resulting in the corresponding variation in catalytic activity for CO_2 reduction. In addition, with increasing Au composition, the binding strength of intermediates on the Au-Pt bimetallic films may still follow the scaling relation, which reveals that electronic effect alone in bimetallic catalysts is likely unable to break the scaling relation to freely tune the binding strength of a certain intermediate without affecting others for achieving a high CO_2 reduction performance. This study shows that a single electronic effect in bimetallic system could not reduce the required overpotential for the dramatically improved catalytic activity for CO_2 reduction to CO, and the atomic arrangement also needs to be taken into account to design a bimetallic catalyst for driving highly selective and efficient CO_2 reduction to CO at the reduced overpotential. In addition, the formation of formic acid in the bimetallic systems at reduced overpotentials indicates that synergistic effects can facilitate reaction pathways for products that are not accessible with the individual components.

Acknowledgements

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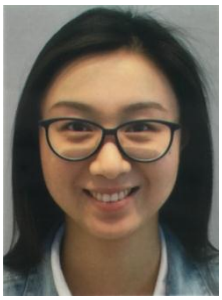

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Research highlights:

· The Au-Pt alloy films were synthesized with tunable compositions for CO2 reduction.

· This tunable catalytic selectivity is linked with the variation of electronic properties caused by changing binary surface composition.

·The d-band center was gradually shifted away from the Fermi level with increasing Au content

·The binding strength of intermediates on the Au-Pt bimetallic films still follows the scaling relation.